

Atomic swelling upon compression

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Abstract. The hydrogen atom under the pressure of a spherical penetrable confinement potential of a decreasing radius r_0 is explored, as a case study. A novel counter-intuitive effect of atomic swelling rather than shrinking with decreasing r_0 is unraveled, when r_0 reaches, and remains smaller than, a certain critical value. Upon swelling, the size of the atom is shown to increase by an order of magnitude, or more, compared to the size of the free atom. Examples of changes of photoabsorption properties of confined hydrogen atom upon its swelling are uncovered and demonstrated.

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Modifications in the structure and spectra of atoms confined in cages whose sizes are commensurable with atomic sizes has been probed by researchers since the early works of Michels *et al* [1] and Sommerfeld and Welker [2] devoted to hydrogen centrally confined in an impenetrable square-well of adjustable radius, to simulate pressure. To date, numerous aspects of the structure and spectra of atoms under various kinds of confinements have been attacked from many different angles by research teams worldwide. This has resulted in a huge array of unraveled effects and data being accumulated in a large number of publications, see reviews [3, 4, 5] as well as numerous review papers in [6, 7] (and references therein). There, one finds a wealth of information on properties of single-electron, two-electron and many-electron atoms confined by impenetrable spherical, spheroidal as well as open boundaries potentials (e.g., see review papers in [6] by Aquino, p.123; Laughlin, p.203; Cruz, p.255; Garza and Vargas, p.241), oscillator potentials (e.g., Patil and Varshni [6], p.1), potentials limited by conoidal boundaries (Ley-Koo E [6], p.79), Debye potentials (Sil, Canuto and Mukherjee [7]), fullerene-cage potentials (Dolmatov [7], p.13; Charkin *et al* [7], p.69), *etc.* All these activities speak to the importance of the subject. This is because confined atoms behave differently from free atoms in ways which provide insight into various interesting problems of interdisciplinary importance. To list a few, the latter could be associated with atoms trapped in hollow cavities of solids, zeolites, fullerenes, helium droplets formed in walls of nuclear reactors, atoms/ions placed in a plasma environment, *etc.* Furthermore, by suitably tailoring the confinement parameters, novel specific atomic properties can be designed in a controllable manner, thereby opening up new technological possibilities for confined atoms.

The aim of this paper is to demonstrate that upon compression of an atom by a suitably tailored repulsive confining spherical potential $U_c(r)$ of a finite height and thickness, the atom can be transformed into novel exotic sort of an atom of a large size and distinct spectra. It is found that upon decreasing the radius of the confining potential (thereby increasing the pressure on a confined atom) below to a certain critical value r_c , the atom stops behaving in the conventional manner. Instead, the atom suddenly swells rather than keeps shrinking in size. This effect is termed *atomic swelling*. It is the ultimate aim of this paper to demonstrate and interpret atomic swelling, as well as to explore trends which might occur in photoabsorption spectra of confined atoms upon atomic swelling. The hydrogen atom is chosen as a touchstone for such a study. Atomic units (a.u.) are used throughout the paper unless otherwise specified.

For confined hydrogen, radial wavefunctions $P_{n(\epsilon)\ell}(r)$ and energies $E_{n(\epsilon)\ell}$ of discrete states $n\ell$ or continuum spectrum $\epsilon\ell$, in the presence of a spherical confinement modeled by a confining potential $U_c(r)$, are determined by a radial Schrödinger equation

$$-\frac{1}{2} \frac{d^2 P_{n(\epsilon)\ell}}{dr^2} + \left[\frac{-1}{r} + \frac{\ell(\ell+1)}{2r^2} + U_c(r) \right] P_{n(\epsilon)\ell}(r) = E_{n(\epsilon)\ell} P_{n(\epsilon)\ell}(r). \quad (1)$$

As a first guiding step in understanding which aspects of a confined/compressed

hydrogen atom (labelled $H@U_c$) are most unusual, $U_c(r)$ is approximated by a square-well potential of certain adjustable inner radius r_0 , height $U_0 > 0$ and thickness Δ , as in [8]:

$$U_c(r) = \begin{cases} U_0 > 0, & \text{if } r_0 \leq r \leq r_0 + \Delta \\ 0 & \text{otherwise.} \end{cases} \quad (2)$$

However, the square-well with infinitely sharp boundaries might be thought to induce some artefacts in the structure and spectra of $H@U_c(r)$. Therefore, a trial study where the square-well potential is replaced by a potential with diffuse boundaries [to be labelled as $U_c^{\text{DP}}(r)$] is conducted in this paper as well. For this, $U_c^{\text{DP}}(r)$ is represented by the sum of two repulsive Woods-Saxon potentials:

$$U_c^{\text{DP}}(r) = \frac{2U_0}{1 + \exp(\frac{r_0 - r}{\eta})} \Big|_{r \leq r_0 + \frac{1}{2}\Delta} + \frac{2U_0}{1 + \exp(\frac{r - r_0 - \Delta}{\eta})} \Big|_{r > r_0 + \frac{1}{2}\Delta}. \quad (3)$$

Here, η is the diffuseness parameter, and r_0 , U_0 and Δ are the same as the parameters of the square-well potential (2). In this paper, the U_0 , Δ and η parameter values are arbitrary chosen to be $U_0 = 2.5$, $\Delta = 5$ and $\eta = 0.5$, just as a case study.

One of key results of the study - atomic swelling upon compression - is demonstrated by figure 1 for the 1s ground-state of hydrogen under compression. First, one can see that the $P_{1s}(r)$ wavefunction of $H@U_c$ gets contracted into the inner region of space as r_0 is decreased from $r_0 = \infty$ (free hydrogen) to $r_0 = 1.59$. The energy E_{1s} , in turn, increased (less binding) from $E_{1s} \approx -13.6$ eV for free hydrogen to $E_{1s} \approx -4.14$ eV for $H@U_c$ at 1.59. Thus far, both $P_{1s}(r)$ and E_{1s} behave in the conventional manner. However, at just a bit smaller r_0 , specifically, at $r_0 = 1.45$ versus $r_0 = 1.59$, the 1s orbital suddenly expands into an outer region in space, gets quite diffuse and peaks at $r \approx 11.5$ or $r \approx 13$, depending on whether the atom is confined by the square-well or diffuse potential, respectively. The implication is that under the increased pressure, when r_0 reaches the value of $r_0 = 1.45$, the atom suddenly swells strongly, rather than getting shrunk, in size - the effect referred to as *atomic swelling* in this paper. At this $r_0 = 1.45$, the atomic size becomes more than by the order of magnitude bigger than the size of the free atom, due to spectacular atomic swelling. A trial calculation showed that further decrease of r_0 hardly affects $P_{1s}(r)$ and E_{1s} ; both of them remain practically unchanged at $r_0 \leq 1.45$. This is because, at $r_0 \leq 1.45$, about all of the 1s electron density has concentrated outside of the confining potential. Therefore, decreasing r_0 below 1.45 cannot exert any more pressure on the atom. Hence, both $P_{1s}(r)$ and E_{1s} stop changing any significantly for all $r_0 \leq 1.45$. Next, the $P_{1s}(r)$ functions, calculated with the use of either the square-well or diffuse confining potential, are almost the same at $r_0 = 1.45$, as is clearly seen in figure 1. This implies that, first, atomic swelling is not an artifact caused by the infinitely sharp boundaries of the square-well potential and, second, atomic swelling is somewhat insensitive to the shape of a penetrable confining potential. For

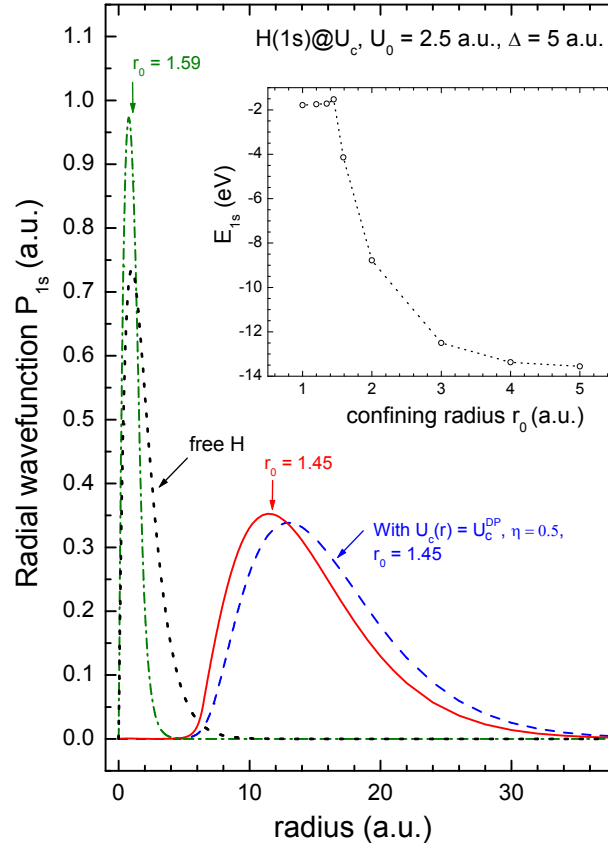


Figure 1. The 1s radial wavefunction $P_{1s}(r)$ of hydrogen confined by a square-well potential with $U_0 = 2.5$ a.u. and $\Delta = 5$ a.u. calculated for $r_0 = 5, 1.59$ and 1.45 a.u., as marked. Also plotted are calculated data obtained with the use of a diffuse confining potential $U_c^{DP}(r)$ with $\eta = 0.5$, as well as data for free hydrogen, as marked. Inset: The 1s electron energy versus the confining radius r_0 of the square-well potential.

this reason, all other calculated data presented in this paper were obtained with the use of the square-well potential, for the sake of simplicity. Interestingly, this effect of atomic swelling is opposite to another counter-intuitive effect of *orbital compression* by *attractive confinement* which was revealed earlier in work [9]. Finally, note, the attempt to calculate $P_{1s}(r)$ and E_{1s} between $1.45 < r_0 < 1.59$ failed, for a reason which is explained later in the paper.

The physics behind the effect discovered, atomic swelling of hydrogen under compression, becomes clear when one explores figure 2, where the effective potential $U_{1s}^{\text{eff}}(r) = -\frac{1}{r} + U_c(r)$ ‘seen’ by the 1s electron in the $\text{H}@U_c$ atom is depicted. One can see that adding the confining potential to the atomic potential makes $U_{1s}^{\text{eff}}(r)$ to consists of two wells, a short-range inner well and shallow long-range outer well. As long as the the confining radius r_0 is such that the inner short-range is more binding than the outer well, the 1s electrons remains in the inner well. There, the atom behaves ‘normally’, i.e., its size is shrinking and the E_{1s} energy rising with decreasing r_0 . However, as the confinement radius r_0 and, hence, the width of the inner short-range well becomes the same or smaller than some critical value, $r_0 \leq r_c$, the inner well becomes less binding,

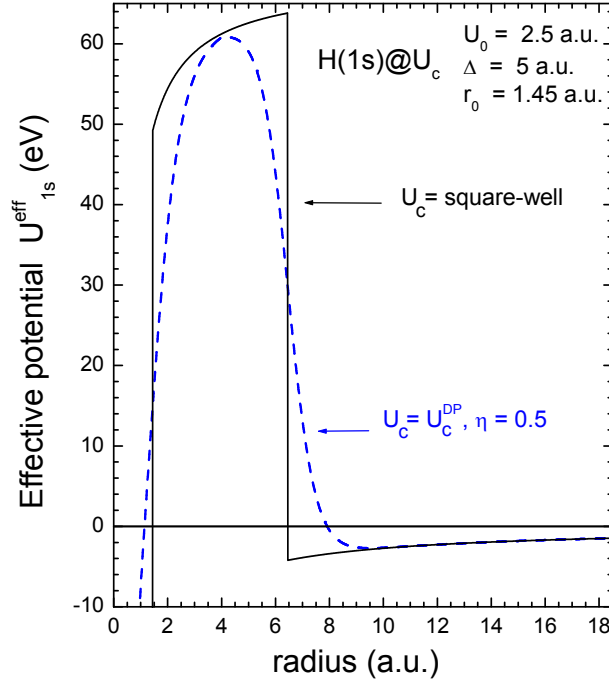


Figure 2. The effective potential $U_{1s}^{\text{eff}}(r) = -\frac{1}{r} + U_c(r)$ “seen” by the 1s electron in the $\text{H}@U_c$ atom when the confining potential U_c is approximated by a square-well potential with $U_0 = 2.5$, $r_0 = 1.45$ and $\Delta = 5$ a.u. (solid line), or diffuse potential U_c^{DP} with $\eta = 0.5$, as marked.

and so the binding of the electron is altered in favour of the long-range outer well. As a result, atomic swelling into the outer well is induced by gradually reducing the confinement radius r_0 to $r_0 \leq r_c$. In the chosen case study, atomic swelling occurred at $r_0 \leq 1.45$. Note, the double-well potential naturally occurs in d- and f-series of free atoms, resulting in the effect known as orbital collapse (a thorough review of the topic was given by Connerade [10], Chapter 5). The difference here is that orbital collapse is due to the centrifugal term in the effective atomic potential, and, hence, affects only states with $\ell \neq 0$, in contrast to the present study. It also results in orbital shrinking rather than swelling. Both situations, however, are clearly similar in the spirit. Furthermore, even closer in the spirit, but opposite in the intention and outcome, was the study performed in [11, 12]. There, atoms with an electron being originally bound by an outer long-range well of the *natural* atomic double-well potential [e.g., an excited $3d^*$ electron in $\text{Cr}(3p^5 3d^5 4s^1 3d^*, ^7P)$], were placed inside a spherical potential of decreasing radius r_0 , with finite or infinite potential height U_0 , but infinite thickness $\Delta \rightarrow \infty$. That resulted in turning the outer long-range well into a short-range well which, thus, became less binding, or otherwise destroyed at all, at small r_0 , for an obvious reason. As a result, the competition between the inner and outer wells was altered in favour of the former, leading to $3d^*$ orbital collapse into the inner well. In the present study, on the contrary, due to *finite* Δ , the double-well potential is artificially *created* rather than getting destroyed as in [11, 12], and not the *outer* well but the *inner* well is shortened

upon decreasing r_0 , so that the competition takes the opposite direction resulting in orbital swelling rather than collapse.

Now, what about the range of $1.45 < r_0 < 1.59$, where the calculation of $P_{1s}(r)$ and E_{1s} failed in the present study? The interpretation is that, for $1.45 < r_0 < 1.59$, both the short-range inner and long-range outer wells have about the same binding strength for the 1s electron. Correspondingly, $P_{1s}(r)$ should possess two maxima of not too dissimilar amplitudes, one in each of the well. Earlier such rare occurrence was found to emerge naturally in nf series of Ba^+ [10, 13] and in compressed Cr [11, 12]. It becomes very difficult to obtain the solution of the Shrödinger or Hartree-Fock equation in this parameter range, where a standard computer algorithm becomes unstable; see discussion of this topic in Chapter 5 of [10], or a brief discussion and references in [11].

Not only can the 1s ground state of confined hydrogen experience atomic swelling, but excited states as well. This is clearly demonstrated by figures 3 and 4, where the P_{2p} and P_{3p} radial functions of hydrogen compressed by the square-well potential with $r_0 = 1.45$ (figure 3) and $r_0 = 1.59$ (figure 4) are depicted. Let us discuss the displayed

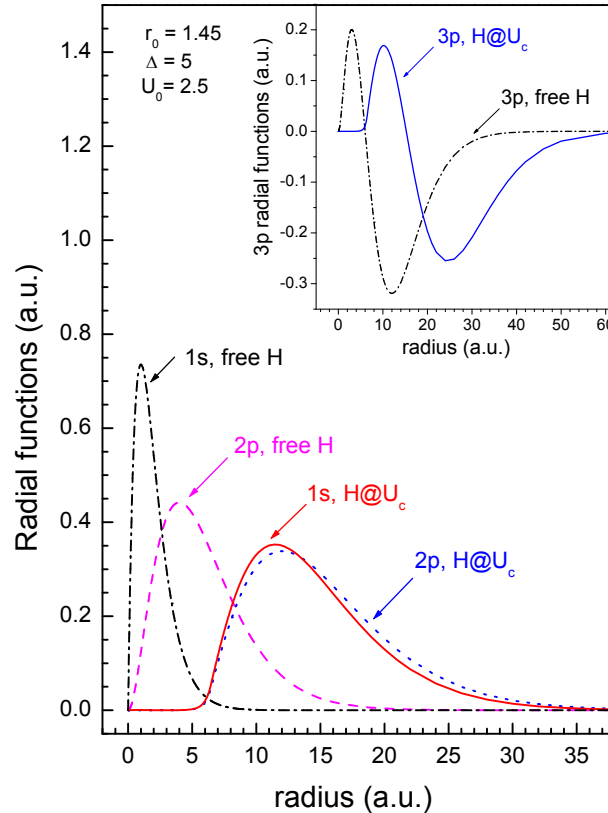


Figure 3. Radial functions $P_{1s}(r)$, $P_{2p}(r)$ and $P_{3p}(r)$ of free hydrogen and hydrogen confined by the square-well potential U_c with $U_0 = 2.5$, $r_0 = 1.45$ and $\Delta = 5$ a.u., as marked.

calculated data for $r_0 = 1.45$ and $r_0 = 1.59$ separately, along with their significance for the photoabsorption spectra of the compressed atom.

Exploring figure 3 ($r_0 = 1.45$), one can see, first, that the excited P_{2p} orbital peaks

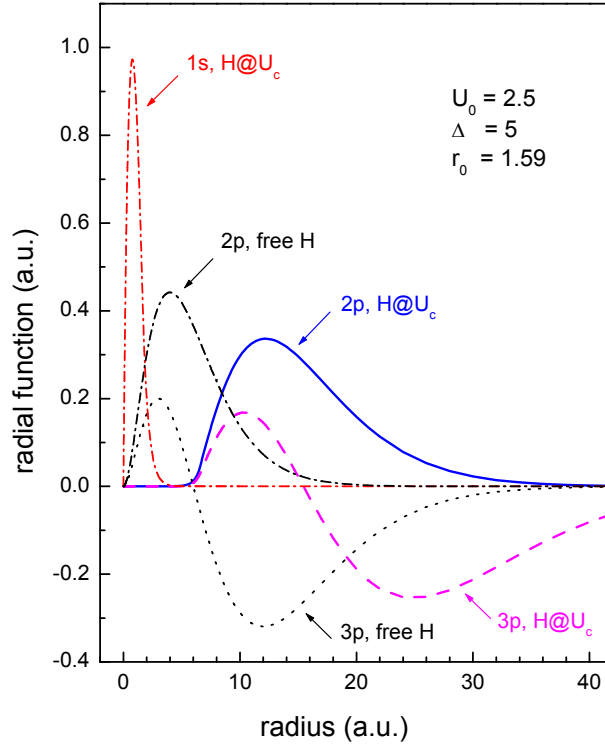


Figure 4. Radial functions $P_{1s}(r)$, $P_{2p}(r)$ and $P_{3p}(r)$ of free hydrogen and hydrogen confined by the square-well potential U_c with $U_0 = 2.5$, $r_0 = 1.45$ and $\Delta = 5$ a.u., as marked.

at $r \approx 12$ versus $r \approx 4$ for free hydrogen. Thus, the size of the $H(2p)@U_c$ atom is three times of the size of the excited free atom - a clear evidence of atomic swelling of excited states under the confinement. Second, highly spectacular, the excited P_{2p} and ground-state P_{1s} functions of $H@U_c$ appear to be about the same and pick at about the same value of r . The overlap between P_{2p} and P_{1s} is thus huge, compared to that of the free atom. This implies an anomaly large oscillator strength $f_{1s \rightarrow 2p}$ of the $1s \rightarrow 2p$ transition in $H@U_c$. Indeed, the calculation shows that $f_{1s \rightarrow 2p} \approx 0.812$ in $H@U_c$ compared to only ≈ 0.416 in free hydrogen. As known, the sum of all oscillator strengths of $n\ell \rightarrow n'(\epsilon)\ell \pm 1$ transitions from an atomic $n\ell$ subshell into its discrete and continuum spectra equals the number of electrons in the subshell. Hence, in our case, over 80% of the total oscillator strength of $H@U_c$ belongs to a single transition $1s \rightarrow 2p$ - a bizarre property of the atom under penetrable confinement. Note, earlier [14, 15], the anomaly large value of $f_{1s \rightarrow 2p} \approx 1$ of hydrogen was predicted upon its confinement inside of an impenetrable well ($U_0 = \infty$, $D = \infty$) of a small radius r_0 . That result, however, is not surprising, since the impenetrable confinement *does* actually compress the atom by driving the $2p$ orbital closer to the $1s$ one.

Looking at figure 4 ($r_0 = 1.59$), one meets another set of unusual results. Indeed, one can see that, due to atomic swelling, the excited P_{2p} and P_{3p} orbitals of $H@U_c$ are, first, pushed far away from the origin, whereas the ground-state function P_{1s} peaks compactly near $r \approx 1$, as in the free atom (1s atomic swelling does not occur at

$r_0 = 1.59$). Thus, second, mostly important, both $P_{2p} \approx 0$ and $P_{3p} \approx 0$ everywhere where $P_{1s} \neq 0$ in $H@U_c$, in contrast to the behaviour of P_{1s} , P_{2p} and P_{3p} in the free atom. Correspondingly, the overlap between P_{1s} and P_{np} functions is practically zero, so that $f_{1s \rightarrow np} = 0$, in the compressed atom. This implies, that the compressed atom has lost its $1s \rightarrow n'\ell \pm 1$ discrete photoabsorption spectrum. Hence, the only possibility for the $H(1s)@U_c$ atom to absorb a photon is exclusively through its photoionization. Thus, the spectra of the free hydrogen, hydrogen under confinement with $r_0 = 1.59$ and hydrogen under confinement with $r_0 = 1.45$ are distinctly different from each other, both qualitatively and quantitatively.

In conclusion, the discussion in the present paper has dealt with the atomic structure and photo-spectra of hydrogen under compression by a repulsive penetrable spherical potential $U_c(r)$ of a certain height U_0 , thickness Δ and inner radius r_0 . The tendency of sudden atomic swelling rather than contraction upon increasing pressure has been discovered. Profoundly distinct impacts of atomic swelling on the photo-spectra of hydrogen under confinement have been demonstrated. Specifically, it has been unraveled that atomic swelling can result either in the loss of a discrete photoabsorption spectrum of the atom, or, on the contrary, in its significant gain, depending on pressure (i.e., the confinement radius r_0). The findings have been exemplified using of arbitrarily chosen values of U_0 and Δ . However, some critical values of U_0 and Δ below which the effects will vanish are anticipated. This will happen when U_0 and Δ are such that the confining potential fails to push atomic levels up to the degree needed for the electron to jump from a narrow inner binding well of the effective potential $U_{1s}^{\text{eff}}(r)$ into its outer binding well (see figure 2), at any r_0 . Other than that, the effects discovered must persist for a broad range of U_0 and Δ values. As a follow-up study, it would be interesting to learn how atomic swelling develops in a multielectron atom, where not just one electron but two or more might jump from the inner well into the outer well of $U^{\text{eff}}(r)$ at a certain critical value of r_0 , how the effect could affect electron correlation in the atom, as well as how all this could modify the interaction of radiation with such a compressed multielectron atom relative to the free atom. The authors are currently working on these topics. As for the present paper, its sole aim has been to demonstrate the existence and importance of atomic swelling itself, as the first step towards the understanding of what might happen in atoms confined by repulsive spherical potentials of finite thickness.

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